The intramolecular rearrangement of β-phenylhydroxylamine to p-aminophenol under pressure

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THE INTRAMOLECULAR REARRANGEMENT OF β-PHENYLHYDROXYLAMINE TO P-AMINOPHENOL UNDER PRESSURE.

By Ryo Kiyama and Shigeru Minomura.

Introduction.

P-aminophenol is manufactured from the intramolecular rearrangment of β-phenylhydroxylamine by the electrolytic reduction of nitrobebzene in a conc sulphuric acid solution. E. Bamberger[1]~[5] and his co-workers have studied this catalyzed intramolecular rearrangement, and found that phenylhydroxylamine is rearranged to *p*-aminophenol with azoxybenzene, aniline and 4-aminophenolsulfonic acid-(2) etc. as byproducts by boiling a dil sulphuric acid solution or by preserving the solution at room temperature for a few weeks or by preserving a conc sulphuric acid solution below 0° C, and discussed the mechanism of the intramolecular rearrangement in conformity to these facts. They also studied the non-catalyzed reaction only by heat and showed qualitatively that phenylhydroxylamine changes to a very small amount of *p*-aminophenol, mostly to azobenzene and water, and at the same time to aniline and azoxybenzene etc. as byproducts.

The authors studied the effect of pressure (0~9,000 atm) on the non-catalyzed intramolecular rearrangement of β-phenylhydroxylamine to *p*-aminophenol at temperatures 75~115° C.

Experimentals.

(1) The materials. Phenylhydroxylamine was prepared by reducing nitrobenzene with ammonium chloride and zinc turnings in accordance with the method of O. Kamm.[6] It was purified two or three times by crystallizing from a ether solution and washing with benzene, till the melting point was found to be 81~81.5° C and preserved in vacuum to be protected from air oxidation.

(2) The determination of *p*-aminophenol. Aminophenol can be determined by jodine-titration[7] of quinonchlorimide which is produced from aminophenol and hypochlorite, but the determination can not be applied because of the disturbance of phenylhydroxylamine. As aminophenol is scarcely soluble in chloroform, and

(1) E. Bamberger, *Ber.*, **27**, 1349, 1548 (1894)
(2) E. Bamberger and J. Lugutt, *ibid.*, **31**, 1500 (1898)
(3) E. Bamberger, *ibid.*, **33**, 3600 (1900), **34**, 61 (1901)
(4) E. Bamberger and A. Riging, *ibid.*, **34**, 229 (1901)
(5) E. Bamberger, *Ann. Chem.*, **390**, 148 (1912)
(6) O. Kamm, *Organic Synthesis*, vol. 4, 57 (1925)
(7) A. D. Powell, *The Analyst*, **44**, 22 (1919)

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phenylhydroxylamine, azobenzene, aniline and azoxybenzene are very soluble, the sample to be weighed was dissolved in the saturated chloroform solution of aminophenol, aminophenol being settled down as the precipitate in the corked tube. Insoluble aminophenol was filtered with a glass filter by suction, dried and weighed. The glass filter was weighed again, after aminophenol was dissolved away with hot methanol. Aminophenol was determined from the difference in the weight measured. More than 0.2 milligrammes of aminophenol could be detected by this method.

(3) **The experimental procedure.** The experiment in vacuum was carried out as follows: a glass test-tube containing about 0.4 gr of phenylhydroxylamine was evacuated, sealed and preserved for a definite time under the conditions of the fixed temperature and the vapour pressure of the sample. The experimental apparatus at high pressures was the same as the reports[8],[9] of *This Journal*. About 0.4 gr of phenylhydroxylamine was compressed in a pressure-proof vessel. About 5 minutes were required for temperature controlling and the intramolecular rearrangement in this lapse of time was within the analytical error. After the sample was preserved for a definite time at the fixed temperature and pressure, aminophenol was determined by the method described above. The data is shown as to the case in which the sample was solid, or partially liquid at the normal temperature after the reaction.

Experimental Results.

The intramolecular rearrangement caused under the conditions of temperatures 75～115°C, pressures 0～9,000 atm and reaction time ½ hour, is shown in Table 1 and Fig. 1. The amount of rearrangement results in a little increase with temperature and pressure. The sample was liquid even at the normal temperature after the reaction in the case denoted by asterisks in Table 1.

Table 1

Temp °C \ Atm	Transition per cent in 1/2 hour					
	0	1	450	2250	5400	9000
75	0.29	0.31	0.36	0.57	0.81	1.02
85	0.36	0.38	0.42	0.62	0.86	1.08
100	*	*	*	0.77	1.01	1.21
115	*	*	*	*	1.11	1.30

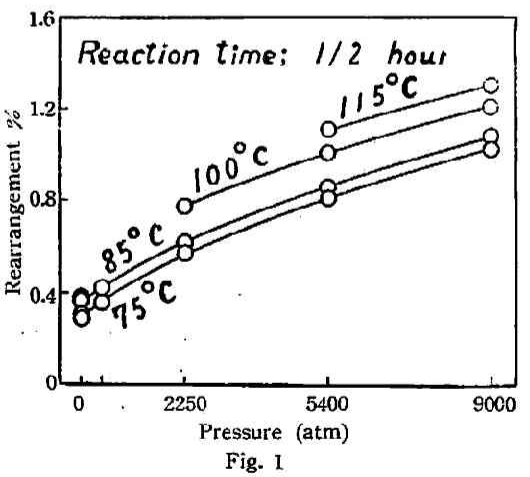


Fig. 1

(8) R. Kiyama, *This Journal*, **19**, 1 (1945)
(9) R. Kiyama and T. Yanagimoto, *ibid.*, **21**, 32 (1951)

The rearrangement under 5,400 atm and in vacuum at 85° C is shown in Table 2 and Fig. 2. The amount of rearrangement under 5,400 atm increases with time and

Table 2

Hour / atm	Transstion per cent at 85° C			
	1/2	1	2	3
0	0.36	0.48	0.53	0.57
5400	0.85	1.21	1.57	1.72

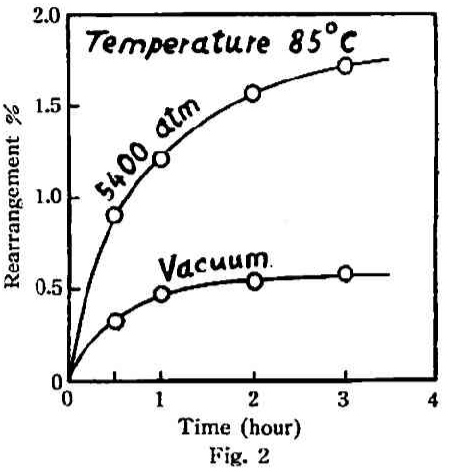


Fig. 2

does not reach equilibrium even in 3 hours, but in vacuum it reaches equilibrium and shows a smaller value than under pressure. The sample was liquid completely at the normal temperature after the reaction for 2 hours in vacuum, but it was partially liquefied after the reaction for 3 hours at 5,400 atm.

Discussions.

The experimental results described above can be summerized as follows:

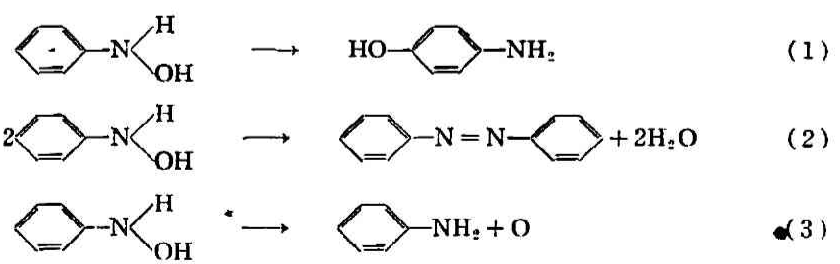
(1) The amount of intramolecular rearrangement for 1/2 hour results in a little increase with temperature and pressure. (Fig. 1)

(2) The pressure effect on the rearrangement increases with time and the rearrangement does not reach equilibrium even for 3 hours. (Fig. 2)

The pressure effect on the chemical equilibrium is expressed by the following equation, which has been discussed in the previous report[10] of *This Journal*,

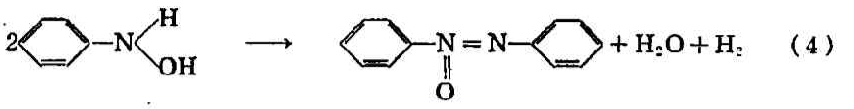
$$\ln\frac{K_p}{K} = -\frac{\Delta V}{RT}P,$$

where K_p and K are the chemical equilibrium constant under a definite pressure and that in vacuum respectively and ΔV is the difference of the molecular volume between the final and initial states of the reaction system. The following reactions have been found as to the non-catalized reaction of phenylhydroxylamine.



(1) (2) (3)

(10) R. Kiyama and S. Minomura, *This Journal*, 22, 4 (1952)



(4)

Therefore, the pressure effect on the intramolecular rearrangement must be discussed, taking into account these reactions. The following facts can be found from the experimental results described above: at the normal pressure the most part of phenylhydroxylamine shows the reactions (2)~(4), and its small part the intramolecular rearrangement to aminophenol of (1) which reaches equilibrium in about 3 hours. The reactions (2)~(4) are retarded by pressure, because the molecular volume in the final state is larger than the initial. On the other hand, not only the rate of reaction but also aminophenol in equilibrium increase by pressure in the reaction (1), although it is a very slow reaction.

Phenylhydroxylamine was compressed too highly to melt in the most experimental data, as the melting point of a material generally shifted to high temperatures with the increase in pressure. The sample was a white solid as it was or liquid partially after the reaction. But the reactions (2)~(4) were accelerated under the conditions denoted by asterisks in Table 1 and the sample showed reddish liquid.

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